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Full Length Research Paper

Compositional differences in the phenolics compounds of muscadine and bunch grape wines

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Wines contain a large array of phenolic compounds, belonging to non-flavonoids, flavonoids and phenolic-protein-polysaccharide complexes. Phenolics in wine are responsible for wine color, astringency, and bitterness. This study evaluates phenolic composition of commercial and experimental wines derived from bunch (*Vitis vinifera*) and muscadine (*Vitis rotundifolia*) grapes to determine compositional differences in phenolics. HPLC analysis of wines showed that majority of phenolic compounds eluted during the first 30 min. Of the red wines tested, Château Cabrières Chateaneuf de Pape (Rhône) showed the simplest phenolics profile while Cabernet Sauvignon (*Vitis vinifera*-California) showed the most complex profile. The phenolics composition of red and white wines varied greatly. Some white wines from bunch grape were devoid of any phenolics. Among muscadine white wines, some contained large number of phenolic compounds while the others showed smaller number of phenolic compounds. These data suggested that both the red and white wines contained a complex mixture of phenolic compounds whose content and composition varied by brand suggesting that the wine processing technique greatly influences phenolics composition of wines than color of the wine. Muscadine red wines were quite distinct than that of the bunch grapes, indicating that grape chemistry has a greater influence on wine phenolic composition.

Key words: Grape, HPLC, phenolics, red and white wines.

INTRODUCTION

Grapes and wine contain a wide spectrum of phenolic compounds. Varietal and flavor characteristics of red wines such as color and tannin characteristics largely are due to the presence of phenolics (Somers, 1971; Noble, 1990; Singleton, 1992). Phenolics affect the sensory characteristics of wines, contributing to bitterness and astringency. Astringency and bitterness are produced primarily by flavonoids that are extracted from the skins and seeds of grapes.

According to Zoecklein et al. (1995), the major phenolic compounds classes in *Vitis vinifera* wines are non-flavonoids or phenolic acids cinnamates and derivatives, low volatility benzene derivatives, tyrosol, volatile phenols, flavonoids (catechins, epicatechins, antho-

cyanins, flavonols, soluble tannin derivatives and other flavonoid derivatives), and tannins or polymerized phenols. These are located in the skins, seeds, and stems, and are higher in red wine than white wine. The flavonoids may exist free or polymerized. These include monomeric flavan-3-ols, such as catechin, epicatechin, anthocyanins, and oligomeric and polymeric flavan-3-ols such as procyanidins. The monomeric and oligomeric flavonoids are substrates of enzymatic as well as non-enzymatic browning in wines, and they brown more intensely than non-flavonoids (Jaworski and Lee, 1987; Lee and Jaworski, 1989). Procyanidins are polymers from catechin and flavan-3, 4-diols (leucocyanidin), and can be found in dimer, trimer, tetramer or other polymer forms (Robichaud and Noble, 1990). The procyanidins are found in the skins and parts of the grape cluster.

Non-flavonoid phenols are derivatives of hydroxycinnamic and hydroxybenzoic acids, such as coumaric (coumaroyl tartaric acid), caffeic (caffeoyl

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tartaric acid), gallic acid, and ellagic acid, as well as other lower molecular weight phenolics. These are the predominant phenols in white wines (Singleton, 1992) since there is minimal contact with skin, stem and seed during the processing of white wines. Zoecklein et al. (1995) reported that the normal light yellow color and the undesirable brown color of white wines are due to phenolics. In young white wine, the yellow color is derived from the limited extraction and oxidation of flavonoids. Also, some of the phenolic acids are browning substrates for polyphenoloxidase and can contribute to browning in white wines when oxidized (Sims, 1994). Therefore the phenolic acids from the pulp are the primary phenols in white wines. The phenolic acids are easily oxidized and contribute to the initiation and control of oxidation in juices and wines. Flavonols, such as quercetin, kaempferol, and myricetin, are localized in grape skin and occur in glycosidic forms. They exist in trace amount in white wines and up to 50 mg/L in young red wines, and approximately 10 mg/L in older red wines (Singleton, 1992).

Complex phenols, also referred to as tannins, are present in high proportion in skins, seeds and stems. These are polymers of both flavonoid and nonflavonoid phenols, which can be hydrolyzable like the ellagitannins or condensed, which are known as procyanidins (Zoecklein, 1995). Polymerization of catechins and leucocyanidins form procyanidins. These polymers range from dimers through decamers, and their molecular weights can be between 500 to 3000. Anthocyanins can also bind to tannins or polymeric phenols, forming anthocyanin-tannin complexes. These complexes have been reported to stabilize the color of *Vitis vinifera* red wines and result in wines that taste less fruity and less astringent after aging (Scudamore-Smith et al., 1990). Generally, their content is not more than 0.80 g/L GAE in white wines and 3.0 g/L in red wines.

Wine color is due to the flavonoids, which are comprised of anthocyanins and procyanidins that serve as precursors to tannins. The degree of polymerization of anthocyanins and tannins is used to determine the chemical age of a wine. Muscadine wines have a low chemical age and, according to Sims and Morris (1985), the incorporation of anthocyanins into tannin polymers in red muscadine wines was low; this consequently causes unstable color. The anthocyanins in red muscadine wines have a lower degree of polymerization compared to the anthocyanins in red *V. vinifera* wines, and this contributes to the poor color stability (Sims and Morris, 1985, 1986). Additionally, progressive alterations in phenolics during conservation, ageing and reaction with anthocyanins produce proanthocyanin products (Dallas et al., 1995; Escribano-Bailon et al. 1996) resulting in subtle changes in color astringency and taste of wine. In a well-aged wine, there is a disappearance of free anthocyanins and tannins (Nagel and Wulf, 1979). Scudamore-Smith et al. (1990) reported that in Cabernet Sauvignon, the

increased polymerization of anthocyanins with tannins might result in improving long-term color stability.

Polyphenolics (vegetable tannin) constitute a distinctive and unique group of higher plant metabolites. Their uniqueness lies not only in their polyphenolic character, but also in their relatively large molecular size (MW up to 20000).

They have been employed in the treatment of inflammation, liver injury, kidney problems, arteriosclerosis, blood pressure, hypertension, nervous and hormonal problems, stomach disorders, ulcers, inhibition of mucous secretions, etc. (Haslam, 1989).

Genetic, cultural, environmental factors can greatly affect the phenolics content and composition of grape, which in turn would influence the wine and juice composition. Because of the perceived health benefits of phenolics, there is a great consumer interest on the phenolics composition of commercial wines. Although phenolics content and composition of wines in general is known, limited reports exist dealing with comparative differences in phenolics composition of commercial wines, especially between bunch and muscadine wines.

In this study we report variation in phenolics content and composition among the commercial wines produced in different parts of the world. In addition, this study also reports phenolic composition of muscadine wines and compares them with the well-known wines from bunch grapes. Since the nature and characteristics of various phenolics found in wine has been reported extensively in the literature, the scope of this study is limited only to comparing the phenolics profiles of selected commercial wines from bunch and muscadine grapes.

Therefore, this study is intended to compare the phenolics profiles of various wines to learn qualitative differences in phenolic composition of wide range of commercial as well as experimental wines. It is believed that the information presented in this report will increase consumer awareness on the wide differences that exist in phenolics composition of domestic as well as imported commercial wines and between muscadine and bunch grape wines sold in the United States.

MATERIALS AND METHODS

Wines

About twenty red and white wines representing the bunch (*V. vinifera*), Florida hybrids and muscadine (*Vitis rotundifolia*) grape market types were purchased from the local liquor stores in Tallahassee, FL as well as from Lake Ridge Wineries, Clermont, FL. The experimental wines were prepared at the Center for Viticulture and Small Fruit Research by Mr. Zhongbo Ren using the muscadine grapes produced at the Center's Vineyard. The wine selections included both the red and white wines from Italy, Spain, Australia, South America, South Africa, Germany, France, California and Florida.

For comparison, a non-grape wine viz. key lime is also included in the study. Wine samples were filtered using a 0.45 µm filter, and

an aliquot of the sample was used to determine the phenolic composition.

High performance liquid chromatography (HPLC)

The HPLC system used was a Waters automated liquid chromatography system comprising a model 410 controller, two Model 510 pumps, a 710 WISP autosampler with sample cooler, a column oven, and Model 490 UV/VIS detector linked to Model 810 Data Handling system. Reversed-phase separations were carried out at 25°C using a 250 mm X 4.6 mm i.d., 4 micron Phenomenex Prodigy 5µm ODS3 100A column fitted with a 4 mm X 3 mm i.d., 5 µm guard cartridge (C18, ODS, Octadecyl) in an integrated holder (Phenomenex). Detector was set at 280 nm. The mobile phase consisted of potassium phosphate dihydrogen (0.01 M) adjusted to

pH 3.05 with O-phosphoric acid (85%) (B) and organic phase 70% acetonitrile (A) in water. A linear gradient was carried out at a flow rate of 1.2 ml per min for 60 min. An equilibration time of 15 min was allowed before each injection.

RESULTS AND DISCUSSION

For comparative purpose, the phenolics data is organized into three groups on the basis of wine color and source. Thus, the first two figures represent the red (Figure 1) and white (Figure 2) wines from bunch grapes while the Figure 3 shows the data for red and white wines from muscadine grapes.

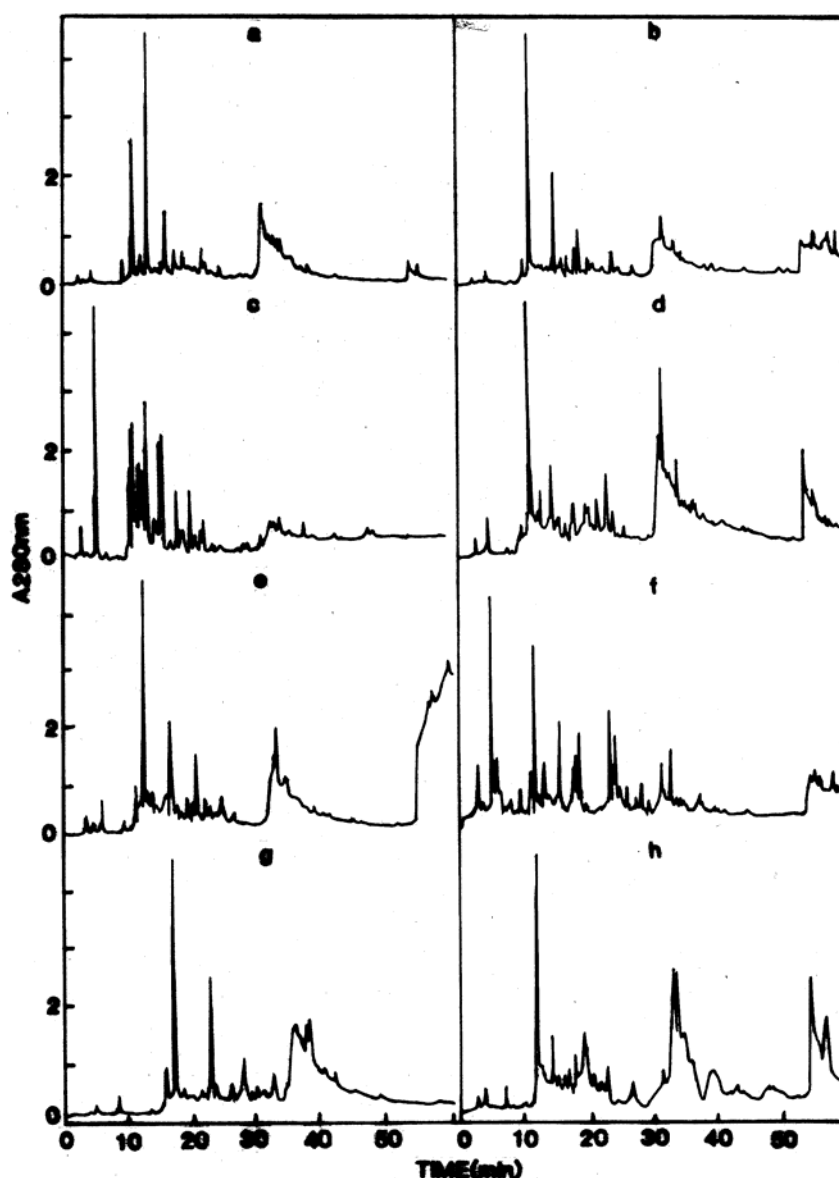


Figure 1. Differences in the phenolic compound composition among the red wines of bunch grape (*Vitis vinifera*). a: Zinfandel, b: Nazzole Chianti Classico Reserva 1998-Italy, c: Cousino Macul Merloth Reserva-South American, d: Zonnebloem Shiraz-South Africa, e: Marques de Murrieta Reserva Red -Spain, f: Cabernet Sauvignon-California, g: Chateau Cabrieres Chateauneuf de Pape 1998 Rhone, h: Chateau Les Grands Chenes 1996-Medoc- Bordeaux.

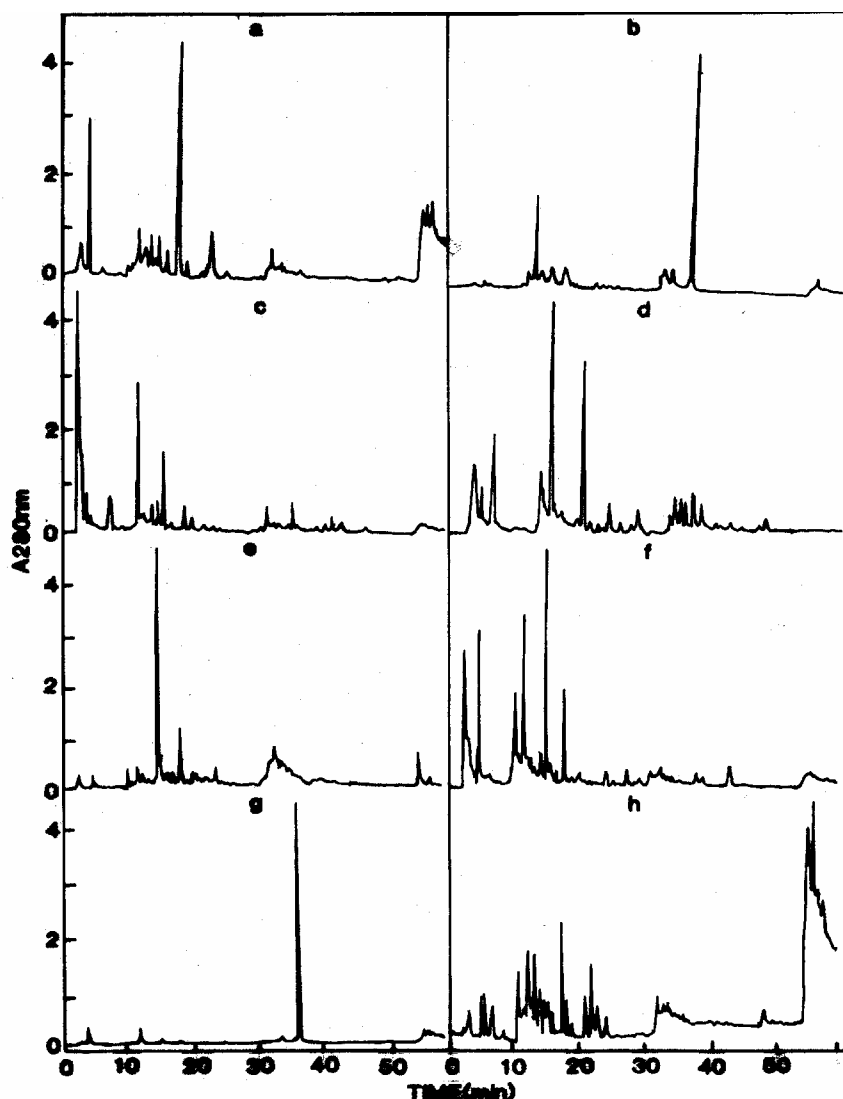


Figure 2. Differences in the phenolic compound composition among the white wines of bunch grape (*Vitis vinifera*). a: Concord-California, b: Claude ChonionChassagne-Montrachet, c: Champaign d: Eugen Wehrhein Niersteiner Oelberg Eiswein-Germany, e: Amerio Moscato D'Asti, f: Louis Mishel Chablis 1999-Chablis, g: Chateau de Coing St. Fiacre Muscadet de S ever et Maine 1998-Loire, h: Key lime.

Bunch Grapes

Red wines: The phenolic profiles of most of the red wines obtained by HPLC was found to be similar (Figure 1). The majority (more than 20) of the phenolic compounds eluted during the first 30 min of the run followed by a group (5 to 7) of moderately resolved compounds eluted between 32 min and 40 min. In Bordeaux (Figure 1h), Zonnebloem Shiraz – South Africa (Figure 1d), and Marques de Murrieta Reserva Red – Spain (Figure 1e) several phenolic compounds (2 to 7) eluted between 50 min and 60 min. In the South America (Cousino Macul Merloth Reserva; Figure 1c) and California (Cabernet Sauvignon; Figure 1f) wines, the phenolic compounds eluting between 32 min and 40 min were either absent or significantly reduced compared to

the other wines indicating that these wines contained lower levels of these compounds. Of the red wines tested, Château Cabrieres Chateaneuf de Pape (Rhône) showed the simplest phenolics profile while Cabernet Sauvignon (California) showed the most complex profile. These data suggested that irrespective of the country of origin, the phenolic profiles of most of the red wines tested were similar and that the variations observed in each wine might reflect compositional differences in grape due to the environment and cultural practices employed in each winery.

White wines: Unlike the red wines, the phenolics composition of white wines varied greatly (Figure 2). Thus Chasagne Montrachet (Burgundy; Figure 2b),

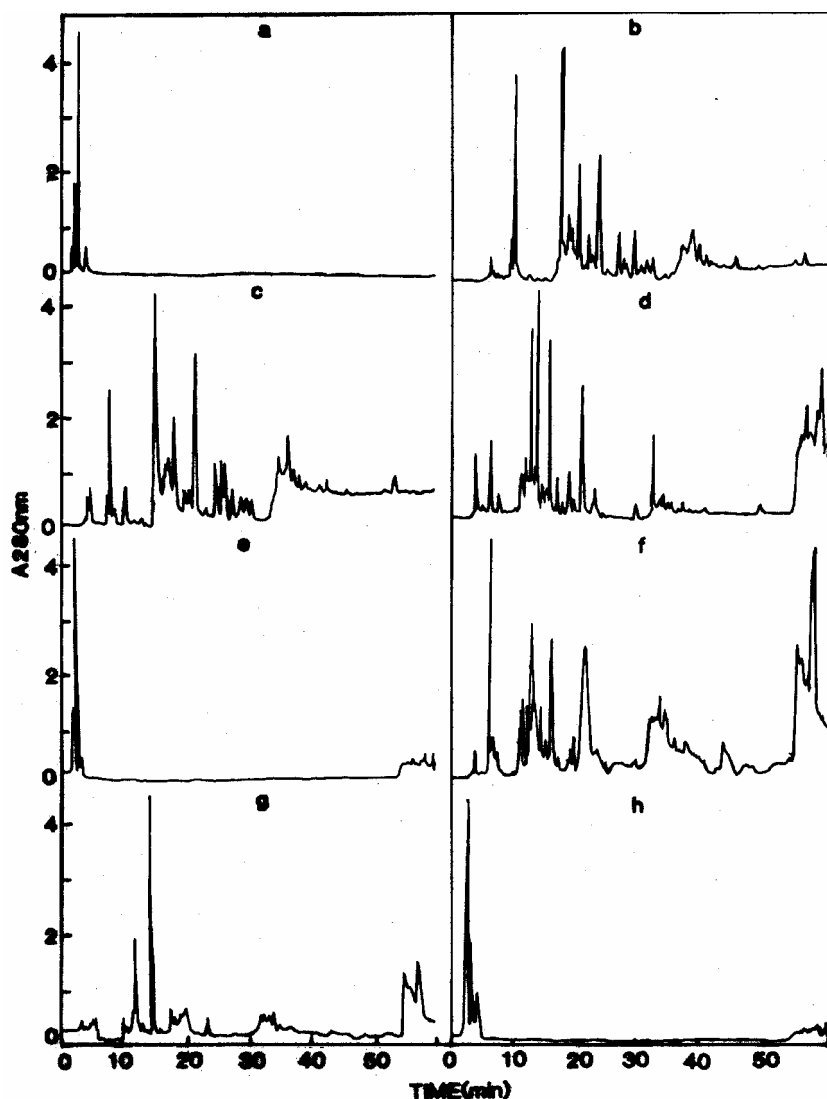


Figure 3. Differences in the phenolic compound composition among the muscadine (*Vitis rotundifolia*) wines. a: Blanc du Bois-White (Lake ridge Wineries, FL), b: Southern Red (Lake ridge Wineries, FL), c: White wine (Florida A&M University), d: Welder-white (Florida A&M University), e: FAMU 99-Red (Florida A&M University), f: Carlos-white (Florida A&M University), g: Southern White (Lake ridge Winery, FL), h: Stover-white (Lake ridge Wineries, FL).

Champaign (Figure 2c), Eugen Wehrhein, Niertheine oelberg, Eiswein (German; Figure 2d), and Louis, Mishel, Chablis (French; Figure 2f), showed more complex phenolic composition followed by Chateau, Coing, St. Fiacre, Muscadet, de Sevre et Maine (Loire; Figure 2g).

Interestingly the phenolic composition of these wines was similar to the red wines suggesting that the phenolics composition of these wines is comparable to the red wines.

This observation suggests that the color of wine may not always reflect its phenolic composition but the fermentation technique and the type of grapes used to produce the wine may greatly influence its phenolic content and composition. However, other white wines viz. Concord (California; Figure 2a), Amerio, Muscato, D'Asti

(Italy; Figure 2e) and Key lime wine (Florida; Figure 2h) showed no phenolic compounds indicating that they were completely devoid of phenolics. This observation further supports that processing technology and the grape genotypes would have major influence on the phenolic content and composition of the wines.

Muscadine wines

Muscadine grapes possess unique characteristics not found in bunch grapes (Olien, 1990). These characteristics include high concentration of certain phenolic compounds and the presence of ellagic acid, which is not ordinarily found in grape species other than

muscadine (Lin and Vine, 1990). Phenolic composition of commercial as well as experimental white and red muscadine wines is shown in Figure 3. In general, the phenolic profile of most of the muscadine wines appeared to be less complex compared to the *V. vinifera* wines. The white wine viz. Stover Reserve 2000 (Lake Ridge Wineries, Clermont, FL) showed most number of phenolic compounds (about 32) followed by Welder and Carlos (about 28; Florida A and M University). Southern White wine (Figure 3g; Lake Ridge Wineries, Clermont, FL) contained least number (one) of phenolic compounds, followed by Southern Red wine (Lake Ridge Wineries, Clermont, FL; Figure 3b).

These data suggested that phenolic compound composition of red and white wines varied greatly. Both the red and white wines contained a complex mixture of phenolic compounds whose content and composition varied by the brand, indicating that the processing technique would greatly influence the phenolic compounds quality and quantity of the wines rather than the color of the grape. In addition, the phenolics profile of most of the red wines prepared from bunch grapes was found to be similar suggesting that the phenolic content and composition of the grape would greatly influence the wine phenolics profile. Interestingly, the red wines made from muscadine genotypes were quite distinct than that of the red wines of *vinifera* indicating that the grape chemistry has a greater influence on wine phenolic composition.

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